



## Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.)

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# Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.)

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Abstract

The accurate reconstruction of sea surface temperature (SST) history in climate-sensitive regions (e.g. tropical and polar oceans) became a challenging task in palaeo-oceanographic research. However, biogenic shell carbonate SST proxies successfully developed for tropical regions often fail in cool water environments. Their major regional shortcomings and the cryptic diversity now found within the major high latitude proxy carrier *Neogloboquadrina pachyderma* (sin.) highlight an urgent need to develop complementary SST proxies for these cool water regions. Here we incorporate the genetic component into a calibration study of a new SST proxy for the high latitudes. We found that the calcium isotopic composition ( $\delta^{44/40}\text{Ca}$ ) of calcite from genotyped net catches and core-top samples of the planktonic foraminifera *Neogloboquadrina pachyderma* (sin) is strongly related to temperature and unaffected by genetic variations. The temperature sensitivity has been found to be 0.17 ( $\pm 0.04$ )‰ per 1°C highlighting its potential for downcore applications in open marine cool-water environments. Our results further indicate that however in extreme polar environments, below a critical threshold temperature of 2.0 ( $\pm 0.5$ )°C and salinity of 33.0 ( $\pm 0.5$ )‰ a prominent shift in biomineralization affect the Ca isotope composition of *N. pachyderma* (sin.) becoming insensitive to temperature. These findings highlight the need of systematic calibration studies to unravel the influencing factors on Ca isotope fractionation and to validate the proxies' applicability.

1 Introduction

The geochemical signatures of carbonate skeletal remains, i.e. foraminifera, corals and bivalves provide a valuable source of information for palaeo-reconstruction of changes in physical and chemical oceanographic conditions. In particular, sea surface temperatures (SSTs) contribute a vital element to our understanding of past and future climate dynamics (Broecker, 1997). Changes in SST strongly impact upon the global

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thermohaline circulation, a major driver of global climate variability on both millennial and orbital timescales (Broecker, 1998). In this context, the polar oceans are of major importance as they represent sensitive key locations of hydrographic activity within the system. The accurate reconstruction of the SST history is therefore essential for climate modelling (Rahmstorf, 2002) yet reliable high-latitude proxies for SST remain elusive.

The growing consensus on the reliability of biostatistical and geochemical SST proxies successfully utilized in the tropics (Rühlemann et al., 1999; Lea et al., 2003; Visser et al., 2003) contrasts markedly with their application in the (sub-) polar oceans. The interpretation of  $\delta^{18}\text{O}$ -values in planktonic foraminiferal shell calcite is complicated by the fact that seawater  $\delta^{18}\text{O}$  is altered significantly by frequent meltwater discharges related to the complex ice-sheet dynamics in this region (Jones and Keigwin, 1988). Moreover, planktonic foraminiferal Mg/Ca ratios show little response to temperature in the Nordic Seas (Meland et al., 2006). This is thought to be due to the difference in seawater carbonate chemistry specifically associated with Arctic polar water masses. These regions are characterised by low salinities and annual sea ice cover. Alkenone proxies overestimate Last Glacial Maximum temperatures for these regions (Rosell-Mele et al., 1999) possibly due to ice-rafted ancient alkenones masking the autochthonous biomarker signal (Weaver et al., 1999). Overestimations are also a common problem in all transfer functions calculated from the near-monospecific assemblages found in polar regions (Pflaumann et al., 1996; Huber et al., 2000; Kucera et al., 2005). These inherent shortcomings highlight the need to develop complementary SST proxies for these high latitude oceans, especially as they are known to act as the pacemaker for glacial-interglacial climate dynamics (Sarner et al., 2001).

Early investigations of Zhu and Macdougall (1998) reported species-dependent variations in calcium isotopic composition in planktonic foraminifera potentially related to temperature. For cultured and field-collected specimens of tropical foraminifer *G. sacculifer* the intra-species variability in  $\delta^{44/40}\text{Ca}$  of approximately 2‰ could have been attributed to temperature differences (Näglér et al., 2000; Hippler et al., 2006). Based

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on these findings the temperature relationship has now been successfully quantified and applied as palaeothermometer in the eastern tropical Atlantic Ocean on glacial-interglacial timescale (Näglér et al., 2000; Hippler et al., 2006). Furthermore, it has been applied to a Caribbean Sea down-core record to reconstruct sea surface temperature and salinity changes in response to the Pliocene closure of the Central American Gateway (Gussone et al., 2004). In high latitudes in turn, left-coiling *Neogloboquadrina pachyderma* (*N. pachyderma* (sin. = sinistral)) strongly dominates planktic foraminiferal assemblages (Kucera et al., 2005; Pflaumann et al., 1996), especially at temperatures below 7–9°C (e.g. Bé and Tolderlund, 1971). Due to its preference for cold-water high-latitude settings on both hemispheres, *N. pachyderma* (sin.) constitutes the major ecological and geochemical proxy carrier in these cooler water environments of palaeoceanographic interest. However, recently published phylogenetic studies have revealed that the morphospecies *N. pachyderma* (sin.) in fact represents several highly divergent genetic types (genotypes) over the Atlantic and Southern Ocean with different biogeographical distributions and environmental adaptations (Darling et al., 2000, 2004, 2006; Stewart et al., 2001; Bauch et al., 2003). It could be shown that the North Atlantic Ocean is inhabited by only one genotype (Type I) whereas the South Atlantic Ocean and the Southern Ocean represent the habitat of four different genotypes (Type II to V). This implies that palaeoceanographic proxies based on this taxon should be calibrated independently.

Several studies clearly demonstrate that Ca isotope fractionation in planktonic foraminifera is strongly species-dependent and should be assessed separately (Skulan et al., 1997; Zhu and Macdougall, 1998). This fact became even more apparent, since Gussone et al. (2003) and Böhm et al. (2006) reported only a slight Ca isotope temperature relationship in biogenic foraminiferal calcite of *Orbulina universa* and aragonite of cultured and open ocean scleractinian corals. In contrast to the pronounced temperature-sensitivity of 0.2‰ per degree Celcius observed for *G. sacculifer*, these relationships are almost an order of magnitude lower than for *G. sacculifer*, but show strong similarities to the slope of temperature-related Ca isotope fractionation in in-

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organic calcite and aragonite precipitates (Gussone et al., 2003; Lemarchand et al., 2004). The reason for this species-dependent bimodal behaviour is still inexplicit pointing to unique and species-related calcification processes, which might be the consequence of the species adaptation to a specific ecological niche. The controversial results of Sime et al. (2005) who analysed 12 species of planktonic foraminifera (including *G. sacculifer*, *O. universa* and *N. pachyderma* (right-coiling)) from core-top sediments observing no significant correlation between temperature and the Ca isotopic composition, have further stimulated the discussion. Their major conclusion is that the theoretically expected relationship between the Ca enrichment factor and temperature can be obscured by, as yet, unquantified metabolic and physiological processes in nature. Nevertheless, recently, high-resolution in situ measurements of the Ca isotope composition on an ion microprobe revealed variations in  $\delta^{44/40}\text{Ca}$  of 1.7‰ within two single tests of 2.8 Ma old *Globorotalia inflata* from Shatsky Rise, ODP leg 198 (Rollion-Bard et al., 2007). The latter authors attributed the intra-test variations to several processes such as ontogenetic effects, differences between primary and secondary calcite and temperature.

Thus the goal of this study is first to examine the Ca isotope fractionation in genotyped *N. pachyderma* (sin.) and compare these results to Ca isotope data obtained from core-top samples of the same species by following two different analytical approaches, and second to investigate the potential of Ca isotope signatures of *N. pachyderma* (sin.) as a complementary tool for multi-proxy SST reconstruction in high-latitude settings. This study should further improve the understanding of how species-dependent temperature sensitivity might be related to different biomineralization processes as a consequence of biological adaptation.

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## 2 Material and methods

### 2.1 Sample locations and material

In this  $\delta^{44/40}\text{Ca}$ -temperature calibration study, we attempt to eliminate the genetically induced uncertainties by using genetically characterised individuals of *N. pachyderma* (sin.). Samples were collected in the northern North Atlantic at 75° N (from 13° W to 13° E). South Atlantic samples were collected along transects between the Falkland Islands (53°21' S, 58° 20' W) and the Antarctic Peninsula (65°36' S, 77°39' W) and samples from the Benguela system were taken offshore Namibia (23° S) (Fig. 1). Samples were obtained either by pumping continually from the surface water layer (6 m, 63- $\mu\text{m}$  filter) or from vertical plankton tows ( $\leq 100$  m, 63  $\mu\text{m}$  mesh). Samples chosen for genetically determinations belong approximately to the 125–250  $\mu\text{m}$  size fraction. On-site sea surface temperature and salinity data were obtained by CTD measurements and ranged between  $-1.0$  and  $14.0^\circ\text{C}$  and 32.5 and 35.0‰, respectively. For more details see Darling et al. (2004).

The study further involved core-top samples of *N. pachyderma* (sin.) from different stations in the Nordic Seas. Sampling sites represent the Norwegian Current, Arctic Domain and polar waters (Fig. 1, inlet A). Four of the core-tops included in this study belong to a group of adjacent core-tops ( $n=35$ ) that were dated by AMS  $^{14}\text{C}$  (compilation of all data in Simstich et al., 2003) and corrected for a  $^{14}\text{C}$  reservoir effect of 400 years (Bard et al., 1994) (Table 2). Most of the core-top dates ( $n=31$ ) are younger than 2500 years before present and can therefore be considered to represent modern conditions, assuming that the major hydrographic parameters in the Nordic seas did not change significantly over this time span (Koç et al., 1993; Sarnthein et al., 2001).

### 2.2 Core-top temperature estimates

High-latitude core top proxy calibrations are limited in their accuracy by several restrictions in “true” calcification temperature estimates, mainly caused by the lack of

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additional independent and robust temperature proxies in these regions. Recently, Nyland et al. (2006) have shown that in a paired  $\delta^{18}\text{O}$  to Mg/Ca down-core proxy approach applied to a sediment core collected in the Norwegian Sea, the  $\delta^{18}\text{O}$ -inferred temperatures are poorly correlated to Mg/Ca ratios, presumably due to short-term variations in  $\delta^{18}\text{O}$  water. Moreover, Mg/Ca ratios derived from planktonic foraminifera of the Nordic Seas are surprisingly insensitive to temperature variations (Meland et al., 2006). Hence, we found that core top calcification temperatures can be best described by modern hydrographic data (e.g. temperature, salinity), which according to Koç et al. (1993) and Sarnthein et al. (2001) have not basically changed in the Nordic Seas over the last 2500 years. Average calcification depths were estimated using the  $\delta^{18}\text{O}$ -difference between shallow-dwelling *Turborotalia quinqueloba* and deeper-dwelling *N. pachyderma* (sin.):  $\Delta\text{depth} = -86 + \Delta\delta^{18}\text{O} \times 300$  (Simstich, 1999). Modern reference temperatures and salinities were then compiled from the World Ocean Atlas (2001) for the inferred depth using available information about the main planktonic bloom (July–September, Kohfeld et al., 1996).

### 2.3 Molecular determinations

Living individuals of polar to subpolar planktonic foraminifera *N. pachyderma* (sin.) were selected for molecular determinations. DNA extraction, amplification by polymerase chain reaction (PCR), cloning and automated sequencing of a ~1000-b.p. region of terminal 3' end of the foraminiferal small subunit ribosomal RNA (SSU rRNA) gene were as described previously (Darling et al., 2000).

### 2.4 Ca isotope analysis

Concerning the genetically characterised material Ca isotope analyses were carried out on single tests of *N. pachyderma* (sin.). These tests were already dissolved in the course of the pre-treatment related to the molecular determination methods. An important advantage of the Ca isotope method applied in both laboratories is the ability

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to measure very small quantities of Ca (200–500 ng). This sensitivity allows replicate analyses of single shells and therefore the innovative approach of performing genetically determination and Ca isotope analysis on the same individual. On the other hand, the analysis of Ca isotopes is a fairly time-consuming method with a limited sample throughput. Therefore, only two or three individuals could have been chosen as representatives for a certain temperature. Concerning the core-top samples approximately 60–80 hand-picked specimens in the size fraction of 125 to 250  $\mu\text{m}$  were selected for isotopic analyses. In this approach potential inter-individual differences become negligible. The shells were crushed between glass plates, cleaned using the Mg-cleaning protocol of Barker et al. (2003) and subsequently dissolved in ultrapure 2.5 N HCl.

Ca isotope analyses were performed on thermal ionization mass spectrometers (TIMS) at the University of Bern (CH) applying a chemical separation and in the stable isotope laboratory at the IFM-GEOMAR, Kiel (D). Both laboratories used a  $^{43}\text{Ca}$ - $^{48}\text{Ca}$  double-spike technique (Näglér et al., 2000; Hippler et al., 2006; Heuser et al., 2002; Gussone et al., 2003). Control runs of selected unspiked core-top samples were measured in sample-standard bracketing technique using an AXIOM multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in the cool plasma mode (Fietzke et al., 2004). As the sample consumption of the MC-ICP-MS is significantly higher we used this method on core locations with sufficient sample material only. Ca isotope variations are expressed in the  $\delta$ -notation:  $\delta^{44/40}\text{Ca} [\text{‰}] = \{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1\} \times 1000$ , where the standard is NIST SRM 915a (Hippler et al., 2003; Eisenhauer et al., 2004). A detailed compilation of various reference materials is available (Hippler et al., 2003). Both laboratories achieve a long-term analytical uncertainty of the standard  $\delta^{44/40}\text{Ca}$  in the order of 0.2 ( $2\sigma$ ) which is equivalent to approximately  $\pm 1^\circ\text{C}$ . The  $2\sigma$  standard deviation of replicate analyses was even lower. Since genetically characterised samples were treated with an EDTA-buffer solution it was essential that samples were treated with a  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  solution prior to and after column chemistry to remove the residual organic compounds (Hippler et al., 2004).

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3 Results

3.1 The Ca isotopic composition of genotyped and core-top samples

The  $\delta^{44/40}\text{Ca}$  [‰] values of *N. pachyderma* (sin.) vary between -0.12 and 1.07 in Arctic specimens (Type I), and between 0.17 and 1.05 in Antarctic specimens (Type III, IV). Samples of the Benguela system (Type V) yield values around 1.75. Core-top  $\delta^{44/40}\text{Ca}$  [‰] values of *N. pachyderma* (sin.) range from 0.36 to 1.05. All Ca isotopic data are presented in Table 1 and 2. The overall intra-species variability in  $\delta^{44/40}\text{Ca}$  of 1.2‰ is six times the uncertainty of the measurements and clearly demonstrates that the Ca isotopic composition of *N. pachyderma* (sin.) is not unique. Given the observations that Ca isotopic composition of seawater is homogeneous throughout modern oceans (Zhu and Macdougall, 1998; Schmitt et al., 2001; Hippler et al., 2003), due to the long residence time of Ca in the ocean ( $\tau=1$  Ma) which is long in comparison to ocean mixing time of approximately 1500 years, these variations do not reflect regional differences in seawater Ca isotopic composition. Small-scale variations of seawater Ca isotopic composition observed in the Early Pleistocene and Late Pliocene of  $\pm 0.2\text{‰}$  compared to the modern seawater value (Fantle and DePaolo, 2005; Heuser et al., 2005) are within the analytical uncertainty and therefore negligible for the purpose of this study.

As mention before, the morphospecies *N. pachyderma* (sin.) could have been subdivided in five highly divergent genotypes, which appear to be adapted to certain environments (Fig. 1). Four of them are included in this study (Type I, III, VI and V) testing a potential inherited genotype dependency on Ca isotope fractionation. However, our findings clearly indicate that the Ca isotopic composition is ambiguous for a certain genotype. Figure 2 illustrates that the respective mean  $\delta^{44/40}\text{Ca}$ -values for genotype I, III and IV, representing temperatures between 0 and 8.5°C, are within uncertainties indistinguishable from each other and are best expressed by the overall weighted average (grey-shaded bar). In addition, the large and similar intra-genotype variability in  $\delta^{44/40}\text{Ca}$  of Type I (net catches and core-tops) and Type III emphasizes that the Ca

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isotopic composition has to be independent from the genotype, but has been likely influenced by an additional, environmental factor. Type V has not been included in the comparison of the mean  $\delta^{44/40}\text{Ca}$ -values, since the samples from the Benguela upwelling region represent mid-latitude environmental conditions, with particularly much higher temperatures, which significantly differ from the high-latitude temperatures characterising the other samples.

### 3.2 The $\delta^{44/40}\text{Ca}$ -temperature relationship of genotyped samples

We observed that the Ca isotopic composition of the calcitic shell of genotyped *N. pachyderma* (sin.) is positively correlated to SST (Fig. 3). We found clear linear trends for genetically characterized specimens collected in the northern North Atlantic and in the South Atlantic above a critical threshold temperature of  $2.0 \pm 0.5^\circ\text{C}$  and salinity of  $33.0 \pm 0.5\text{‰}$ . Considering the analysed genotyped specimens of both hemispheres as independent sample sets has enabled us to calculate the following  $\delta^{44/40}\text{Ca}$ -temperature relationships using the ISOPLOT software by Ludwig (2003).

- 1) For modern specimens of *N. pachyderma* (sin.) of the northern North Atlantic (Type I) the  $\delta^{44/40}\text{Ca}$ -temperature relationship can be expressed as follows:

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.23(\pm 0.06) \times \text{SST}[^\circ\text{C}] - 0.46(\pm 0.26) \quad (1)$$

- 2) For high-latitude South Atlantic specimens of *N. pachyderma* (sin.) (Type III) it can be expressed as:

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.12(\pm 0.05) \times \text{SST}[^\circ\text{C}] - 0.00(\pm 0.29) \quad (2)$$

- 3) For South Atlantic specimens of *N. pachyderma* (sin.) including individuals of the Benguela system (Type V) it can be expressed as:

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.13(\pm 0.02) \times \text{SST}[^\circ\text{C}] - 0.00(\pm 0.16) \quad (3)$$

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To date, the determination of the foraminiferal genotype is restricted to living organisms. However, down-core studies are based on fossil material which could be determined only on the morphospecies level. In consideration of the fact that it would be desirable to develop a morphospecies-based  $\delta^{44/40}\text{Ca}$ -thermometer for high-latitude SST reconstruction, which would be valid down to temperatures of  $2.0 \pm 0.5^\circ\text{C}$ , we further determined the  $\delta^{44/40}\text{Ca}$ -temperature relationship for pooled high-latitude specimens from both hemispheres.

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.17(\pm 0.04) \times \text{SST}[^\circ\text{C}] - 0.21(\pm 0.18) \quad (4)$$

Here, the three specimens from the Benguela system are purposely excluded, since they depict a rather small set of samples and might represent different water mass properties (nutrients, carbonate ion concentration) of a mid-latitude setting. The independent test how Eq. (4) would change, if samples from the Benguela upwelling would have been included, has revealed that it would be indistinguishable from Eq. (4).

$$\delta^{44/40}\text{Ca}[\text{‰}] = 0.16(\pm 0.03) \times \text{SST}[^\circ\text{C}] - 0.18(\pm 0.15) \quad (5)$$

### 3.3 Core-top temperatures based on $\delta^{44/40}\text{Ca}_{\text{core-tops}}$ ( $T_{\delta 44/40\text{Ca}}$ )

The Ca isotopic composition of core-top *N. pachyderma* (sin.) samples collected in the Norwegian Sea is also positively correlated to their corresponding estimated temperatures ( $T_{\text{WOA}}$ ), ranging from 2.5 to 7.0 ( $\pm 1.0$ )  $^\circ\text{C}$ . Furthermore, it has been found that  $T_{\delta 44/40\text{Ca}}$  of core-top samples, calculated from Eq. (4), is within uncertainties in agreement with  $T_{\text{WOA}}$ . Based on the studies of Darling et al. (2000, 2004) we can assume that Holocene core-top specimens of *N. pachyderma* (sin.) collected from the North Atlantic Ocean represent only one genotype, which in turn admits the direct comparison of core-top and genotyped sample sets.

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### 3.4 The “cold-end” paradox

Modern and core-top samples originated from polar and Arctic Domain waters characterised by temperatures below 2.0 ( $\pm 0.5$ )°C and salinities below 33.0 ( $\pm 0.5$ )‰, herein after referred to as samples collected at the “cold-end” plot offset from their respective trendlines. Calculated temperatures based on their Ca isotope ratios would overestimate local temperatures. Our data indicate that the breakdown of the  $\delta^{44/40}\text{Ca}$  to temperature relationship only occurs in these extreme low-temperature and low-salinity environments which are exclusively characterised by the occurrence of almost monospecific foraminifera assemblages (Pflaumann et al., 1996; Kucera et al., 2005).

## 4 Discussion

Our approach to study the Ca isotope composition of genotyped *N. pachyderma* (sin.) in relation to SST and compare it to the Ca isotope composition of *N. pachyderma* (sin.) taken from core-top samples indicates that Ca isotope fractionation seems to be controlled by ambient water temperature. This has been shown particularly for open marine high-latitude settings, with hydrographic conditions above a critical threshold temperature and salinity. Concerning the genotyped samples, for which direct salinity data is available, the range in salinity would have been too small to have a significant impact on the  $\delta^{44/40}\text{Ca}$ -temperature relationship. Based on the fact that *N. pachyderma* (sin.) is the dominating species in high-latitude marine environments, these findings highlight the potential of *N. pachyderma* (sin.) as proxy carrier. It further implies that their Ca isotope records could be used for the reconstruction of SST in open marine high-latitude settings that are not disturbed by seasonal anomalies (e.g. sea ice cover, brine formation). The application of the  $\delta^{44/40}\text{Ca}$ -temperature relationship (Eq. 4) to core-top  $\delta^{44/40}\text{Ca}$  values of the Norwegian Current reflect realistic calcification temperature estimates compared to modern oceanographic data.

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## 4.1 Genetic coherences

The determination of the genotype and  $\delta^{44/40}\text{Ca}$  on the same shell of *N. pachyderma* (sin.) provides direct evidence that genotype does not influence the temperature sensitivity of Ca isotope fractionation. Concerning the samples that were collected above a critical threshold temperature ( $\geq 2^\circ\text{C}$ ) and salinity ( $< 33\text{‰}$ ), Arctic and Antarctic genotyped samples describe the same relationship within analytical uncertainties (see Eq. 4). Even samples of the mid-latitude Benguela genotype fall on this regression. The most significant consequence of the genotype-independency is the global validity of the  $\delta^{44/40}\text{Ca}$ -temperature calibration for down-core studies where sample classifications can only be carried out on the morphospecies level. Thus, even if there would be more than one genotype in the Arctic realm, genotype differences or shifts would have no or only a negligible impact on temperature reconstructions from core-top or down-core studies.

## 4.2 Preservation of shell material

In contrast to pristine genotyped foraminifer shells, core-top shells could incorporate secondary information since they could have been exposed to post-depositional processes. The consistency of  $T_{\text{WOA}}$  and  $T_{\delta^{44/40}\text{Ca}}$  of core-top shell samples from the Norwegian Current confirms that the Ca isotopic composition of foraminiferal calcite is well preserved in these samples and records the primary temperature signal. Particularly crucial for the fossil record, our findings support earlier observations on the preservation potential of *N. pachyderma* (sin.). Investigating foraminiferal distribution and ecology, Martinez et al. (1998) found *N. pachyderma* (sin.) resistant to dissolution. Further evidence of primary signal retention is provided by partial dissolution experiments performed on shells of *N. pachyderma* (sin.) demonstrating that the degree of dissolution has no significant impact on the  $\delta^{44/40}\text{Ca}$  values (Hönisch et al., 2002).

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### 4.3 Calcification depth vs. sea surface temperature

Most observations suggest that *N. pachyderma* (sin.) calcifies at depth similar to other morphospecies used as recorders of SST. There is a general consensus that the vertical distribution of *N. pachyderma* (sin.) is related to local hydrography. An early direct study of the depth habitat of *N. pachyderma* (sin.) demonstrated that it lives above 100 m depth north of 83° N in the Arctic Ocean (Carstens and Wefer, 1992). Peak abundances of *N. pachyderma* (sin.) were observed in the surface 20–80 m in the Northeast Water Polynya (East Greenland Current), in conjunction with the chlorophyll maximum zone (Kohfeld et al., 1996), which is in agreement with  $\delta^{18}\text{O}$  signatures suggesting that *N. pachyderma* (sin.) calcifies in the upper 25 m of the water column offshore Greenland (Simstich, 1999). The assumption of a depth habitat by proxy is the inherent weakness in such core-top calibrations where summer SSTs for the respective core locations are calculated using estimated calcification depths. Further, core-top calibrations suffer from the sites' natural variability integrated over several hundred years. The recalculation of calcification temperatures of core-top specimens of *N. pachyderma* (sin.) by using the  $\delta^{44/40}\text{Ca}$ -temperature relationship based on genotyped specimens (Eq. 4) independently re-assesses the estimated calcification temperatures (Simstich et al., 2003) for the core-top sites and provide strong evidence that they are within the correct range.

### 4.4 Interspecies comparison

The observed  $\delta^{44/40}\text{Ca}$ -temperature sensitivity of *N. pachyderma* (sin.) is similar to the one recently reported for modern specimens of planktonic foraminifera *G. sacculifer* (Hippler et al., 2006) (Fig. 3), which has been successfully applied to down core records in the eastern tropical Atlantic (Hippler et al., 2006) and in the Caribbean Sea (Gussone et al., 2004) to reconstruct temperature and salinity changes on two different geological timescales (Pleistocene and Paleogene). However, the respective trendlines of the temperature sensitivity are significantly offset (Fig. 4a), which emphasises

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the importance of species-specific calibrations for absolute temperature reconstruction. These findings render strong evidence that biocalcification in these two species is related to comparable biochemical mechanisms controlling Ca isotope fractionation.

Although *N. pachyderma* (sin.) and *G. sacculifer* have different ecologies demonstrated particularly in opposite temperature preferences (Zaric et al., 2005), the occurrence of both species is restricted to narrow temperature habitats. According to the SST ranges of some contemporary planktonic foraminifera, illustrating their preferred temperature habitat, *N. pachyderma* (sin.) shows highest relative abundances at the lower temperature limit, corresponding to high-latitude environments, while *G. sacculifer* represents the upper temperature limit characteristic for tropical environments. The species' adaptation to either the lower (cold-end) or the upper temperature limit (warm-end) might explain the development of similar calcification strategies.

In contrast, most other planktonic foraminifera species studied so far, dwelling in subpolar to transitional to subtropical temperate waters, are much less sensitive to temperature (e.g. Gussone et al., 2003; Heuser et al., 2005; Sime et al., 2005). A detailed study on the temperature sensitivity of *Orbulina universa* resulted in a temperature gradient one-order-of-magnitude smaller than that of *N. pachyderma* (sin.) and *G. sacculifer* (Gussone et al., 2003) but similar to the gradient observed for inorganic precipitates. According to the latter authors foraminiferal species could be divided in two distinct groups using different calcification mechanisms. The different Ca fractionation behaviour has been explained by different modes of Ca transport at the site of calcification, either as hydrated  $\text{Ca}^{2+}$  ions in the case of *O. universa* or as dehydrated  $\text{Ca}^{2+}$  ions in the case of *G. sacculifer*. Another theory favoured equilibrium dynamics for Ca isotope fractionation which is based solely on the results obtained for inorganic calcite precipitates (Marriott et al., 2004). The similarity of Ca isotope fractionation in inorganic precipitates and *O. universa* was attributed by these authors to similar equilibrium processes. The stronger temperature dependence of *G. sacculifer* is interpreted as the result of superimposed additional biological fractionation effect assuming different biomineralization processes for both species.

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The temperature sensitivity of Ca isotopes has also been investigated in other important proxy carriers (e.g. coccoliths and corals). Gussone et al. (2006) studied the cellular calcium pathways and isotope fractionation in *Emiliania huxleyi*. They concluded that the main factor influencing Ca isotopes in coccoliths is the isotopic composition of the seawater. The second parameter that affects Ca isotope fractionation ( $\delta^{44/40}\text{Ca}$ ) was temperature, with a small sensitivity of 0.027‰/°C. They further suggested that small variation in Ca isotope composition of coccoliths might be introduced by changes in ambient  $[\text{CO}_3^{2-}]$  or  $p\text{CO}_2$ , which can be neglected for palaeoceanographic reconstruction purposes. Studying cultured and open ocean scleractinian corals, Böhm et al. (2006) found coral Ca isotope composition positively correlated to temperature. The weak temperature sensitivity was similar to inorganic aragonite. However,  $\delta^{44/40}\text{Ca}$  of the coral aragonite was significantly offset from inorganic aragonite, which was best explained by biologically induced fractionation as corals actively transport calcium to the site of calcification.

Insensitivity of Ca isotope fractionation to temperature was recently reported for 12 species of planktonic foraminiferal species collected from core-top sediments (Sime et al., 2005). *N. pachyderma* (sin.) was not included in their study. The authors concluded that any temperature relationship is obscured by yet “unquantified metabolic and physiological processes in nature”. Samples were collected from a suite of box-cores from sites between 60° N and 30° S in the North Atlantic and the West Indian oceans. SSTs ranging from of 9 to 27°C were inferred from  $\delta^{18}\text{O}_{\text{calcite}}$  values of the shells and estimated  $\delta^{18}\text{O}_{\text{seawater}}$  values of seawater for the respective core locations, and therefore incorporate a higher degree of uncertainty ( $\pm 2^\circ\text{C}$ ). Given the broad temperature range, the interspecies variability in  $\delta^{44/42}\text{Ca}$  of 0.6‰ obtained by MC-ICP-MS as well as the minor intraspecies variability of  $\leq 0.1\text{‰}$  (e.g. *O. universa*, *G. sacculifer* and *G. inflata*) could not be attributed to inferred SST. Remarkably, even the inorganic slope (Gussone et al., 2003; Lemarchand et al., 2004) appeared to be obscured in these core-top samples.

Unexpectedly, their findings are inconsistent with recent studies on *G. sacculifer* for

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which a strong temperature response has been reported in cultures, catches and sediments (Nägler et al., 2000; Hippler et al., 2006). Further evidence for the temperature sensitivity of Ca isotope fractionation comes also from ODP site 999 in the Caribbean Sea (Gussone et al., 2004) and from the western equatorial Pacific box core ERDC92 (2°13.5' S, 156°59.9' E Java plateau) (Zhu and Macdougall, 1998), the latter reporting a difference in  $\delta^{44/40}\text{Ca}$  of 0.6‰ between Holocene and Last Glacial Maximum (LGM) samples of *G. sacculifer*. Applying the  $\delta^{44/40}\text{Ca}$ -temperature calibration based on *G. sacculifer* (Hippler et al., 2006) this value would correspond to a temperature change of  $2.7 \pm 0.6^\circ\text{C}$  between the LGM and the Holocene. Furthermore, a consistent SST change for this period of  $2.8 \pm 0.7^\circ\text{C}$  has been estimated for the equatorial Pacific (including data from Java plateau ODP core 806B at 0°19.1' N, 159°21.7' E) based on Mg/Ca ratios in foraminifera (Lea et al., 2000) rendering strong support for a preserved temperature signal in the *G. sacculifer* data (Zhu and Macdougall, 1998).

The reasons for these contrasting Ca isotope fractionation patterns observed in different planktonic foraminifera and other marine species remain a highly interesting challenge for future research. Especially, recent technical achievements have demonstrated that the discussion is not yet brought to an end. Using an ion microprobe, high-resolution in situ measurements of Ca isotope composition have yielded  $\delta^{44/40}\text{Ca}$  values between 0.3 and 2.0‰ within two single tests of planktonic foraminifera *Globorotalia inflata*, dated 2.8 Ma from Shatsky Rise (ODP leg 198, Rollion-Bard et al., 2007). The authors attributed the observed intratest variations to several processes such as temperature variation, ontogenetic effects or differences between primary and secondary calcite, precipitated by different biomineralization processes.

#### 4.5 Ca isotope fractionation at the “cold-end”

$\delta^{44/40}\text{Ca}$  values from genotyped and core-top samples collected in polar surface waters and the low saline Arctic Domain, which are characterised by temperatures below  $2.0 \pm 0.5^\circ\text{C}$  and low salinities (<33‰) were found to plot offset from the trendline of

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the  $\delta^{44/40}\text{Ca}$  temperature relationship (Eq. 4). Calculated temperatures for core-top samples using Eq. (4) seem to become ambiguous and overestimate temperatures in comparison to  $T_{\text{WOA}}$ . Our data indicate that the breakdown of the  $\delta^{44/40}\text{Ca}$  temperature relationship only occurs in these extreme low-salinity environments. The failure of *N. pachyderma* (sin.) as proxy carrier in these extreme environments remains inexplicit. Therefore, a parallel study was performed by Kozdon (2007) applying a multi-proxy approach ( $\delta^{44/40}\text{Ca}$ ,  $\text{Mg/Ca}$ ,  $\delta^{18}\text{O}$ ) to *N. pachyderma* (sin.) tests from Holocene core-tops originating from the Nordic Seas (Norwegian Sea, Arctic Domain). On the basis of the geochemical signatures tests of *N. pachyderma* (sin.) have been subdivided into two groups which differ significantly in their suitability as temperature proxy carrier.  $\delta^{44/40}\text{Ca}$  values and  $\text{Mg/Ca}$  ratios of samples from the Norwegian Sea are positively correlated with temperature and match existing  $\text{Mg/Ca}$  and  $\delta^{44/40}\text{Ca}$  temperature relationships. By contrast, samples from the low saline Arctic Domain result in aberrant  $\delta^{44/40}\text{Ca}$  values and  $\text{Mg/Ca}$  ratios insensitive to temperature differences. These findings have been explained by temperature-dependent proportions of two calcite phases formed by different calcification pathways (cf. Bentov and Erez, 2006), meaning to inhibit the decrease of the  $\text{Mg}$ -content below a certain limit set by the foraminiferal physiology whereas lowest  $\text{Mg/Ca}$  and  $\delta^{44/40}\text{Ca}$  ratios (in core top samples) are observed at the transition between the Norwegian Sea and Arctic Domain waters.

## 5 Conclusions

Conducting systematic  $\text{Ca}$  isotope analyses on tests of *N. pachyderma* (sin.) covering a temperature range between 0 and  $14^\circ\text{C}$  provide a new complementary SST proxy for open marine high-latitude oceans. This is supported by evidence from both genotyped plankton and core-top sediment. A change in  $\delta^{44/40}\text{Ca}$  [‰] of  $0.17 (\pm 0.04)$  corresponds to a temperature change of  $1^\circ\text{C}$ . The temperature sensitivity is indepen-

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dent of genetic variation observed within the major high-latitude proxy carrier highlighting its potential for downcore applications in open marine cool-water environments. We propose to use the  $\delta^{44/40}\text{Ca}$ -temperature relationship, with  $\delta^{44/40}\text{Ca} [\text{‰}] = 0.17 (\pm 0.04) \times \text{SST} [^{\circ}\text{C}] - 0.21 (\pm 0.18)$ , for future applications. The strong temperature sensitivity of Ca isotope fractionation observed above a critical threshold temperature of  $2.0 (\pm 0.5)^{\circ}\text{C}$  and salinity of  $33.0 (\pm 0.5)\text{‰}$  is in excellent agreement with the temperature sensitivity obtained for tropical planktonic foraminifera *G. sacculifer*. Therefore our findings render strong evidence that biocalcification in these two species is related to comparable biochemical mechanisms controlling Ca isotope fractionation. The failure of *N. pachyderma* (sin.) as proxy carrier can be attributed to shifts in elemental and isotopic processing (uptake and removal) during biomineralization and seems to be restricted to extreme polar environments.

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**Table 1.** Calcium isotopic composition of genotyped *N. pachyderma* (sin.).

Northern Atlantic Ocean, <i>Polarstern</i> (ARK XV/1, 1999)									
Station	No.	Longitude [° E/W]	Latitude [° N]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
A5	3	4 17.08E	79 3.73	Type I	33.5	1	0.51	0.13	2
	4	4 17.08E	79 3.73	Type I	33.5	1	0.67	0.2	1
B5	1	2 31.00E	79 7.14	Type I	33.4	2	0.04	0.19	1
	2	2 31.00E	79 7.14	Type I	33.4	2	-0.01	0.16	1
C5	3	2 31.00E	79 7.14	Type I	33.4	2	-0.04	0.21	1
	4	2 31.00E	79 7.14	Type I	33.4	2	-0.12	0.18	1
D5	1	2 59.71 E	79 28.15	Type I	33.7	2	-0.04	0.19	1
F5	2	12 44.72 W	74 59.49	Type I	32.7	2.5	0.27	0.13	1
	3	12 44.72 W	74 59.49	Type I	32.7	2.5	0.36	0.3	1
H5	3	7 23.80 W	75 0.08	Type I	34.8	4	0.45	0.23	1
I5	2	3 33.82 W	75 0.84	Type I	34.8	4	0.54	0.22	1
J5	2	0 22.17 E	75 0.21	Type I	34.7	3.5	0.14	0.2	2
K5	5	5 9.05 E	75 1.06	Type I	35	6.5	1.07	0.24	1
L5	1	10 37.25 E	74 59.66	Type I	35.1	6.5	1.07	0.2	1
M5	1	12 33.57 E	75 0.39	Type I	35	6	0.87	0.18	1
Southern Atlantic Ocean, British Antarctic Survey <i>James Clark Ross</i> (JR 48, 2000)									
Station	No.	Longitude [° W]	Latitude [° S]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
8	69	60° 53'	54° 81'	Type III	34.1	7	0.89	0.25	1
	71	60° 53'	54° 81'	Type III	34.1	7	1.05	0.16	1
10	121	60° 79'	55° 22'	Type III	33.9	6	0.88	0.25	1
	129	60° 79'	55° 22'	Type III	33.9	6	0.92	0.08	2
13	165	64° 31'	57° 98'	Type III	33.9	4	0.53	0.24	1
17	223	65° 32'	61° 00'	Type III	33.7	3.5	0.47	0.2	1
23	265	63° 74'	63° 92'	Type III	33.7	2	0.17	0.3	1
30	297	58° 45'	62° 63'	Type III	34.3	2.5	0.27	0.3	1
36	309	59° 61'	64° 74'	Type IV	32.4	0	0.67	0.19	1
	313	59° 61'	64° 74'	Type IV	32.4	0	0.57	0.21	1
	321	59° 61'	64° 74'	Type III	32.4	0	0.52	0.14	1
	649	56° 75'	52° 21'	Type III	34	8.5	0.80	0.01	2
	651	56° 75'	52° 21'	Type III	34	8.5	0.91	0.15	1
Benguela System (offshore Namibia), <i>RV Welwitscha</i> (2001)									
Station	No.	Longitude [° E]	Latitude [° S]	Genotype	SAL [‰]	SST [°C]	$\delta^{44/40}\text{Ca}$ [‰] <sup>a</sup>	2SD	N
10	13	14 13.26	23	Type V	35	13.5	1.67	0.22	1
	23	14 23.26	23	Type V	35	13.5	1.79	0.26	1
20	35	14 02.45	23	Type V	35	14	1.85	0.29	1

<sup>a</sup>  $\delta^{44/40}\text{Ca}$  values are given in [‰] relative to NIST SRM 915a. Samples were collected either by pumping continually from the surface water layer (6 m, 63- $\mu\text{m}$  filter) or from vertical plankton tows ( $\leq 100$  m, 63  $\mu\text{m}$  mesh).

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**Table 2.** Calcium isotopic composition of *N. pachyderma* (sin.) from Holocene core-tops, Nordic Seas.

Nordic Seas (Norwegian Current) core tops samples										
Core <sup>a</sup>	Longitude [° E/W]	Latitude [° N]	Water depth [m]	$\Delta\delta^{18}\text{O}_{\text{Nps-Tloba}}$ <sup>b</sup>	Inferred depth [m] <sup>b</sup>	SAL [‰] <sup>c</sup>	SST [°C] <sup>c</sup>	$\delta^{44/40}\text{Ca}$ [‰] <sup>d</sup>	n <sup>e</sup>	2SEM <sup>f</sup>
23071-1	2 54.60E	67 04.80	1306	0.53	150–200 m	35.1	6.1	0.64	11	0.11
23259-3	9 18.00E	72 01.20	2518	0.66	150–200 m	35.1	4.8	0.65	4	0.03
23261-2	13 06.60E	72 10.80	1667	0.44	100–150 m	35.0	5.1	0.54	4	0.21
23514-3	25 57.00W	66 40.20	713	−0.05	0–50 m	33.8	4.8	0.55	2	0.14
23523-3	30 13.20W	62 15.00	2156	1.88	>250 m	35.1	6.3	1.05	2	0.16
23528-3	28 50.40W	63 09.60	1632	1.79	>250 m	35.0	6.4	0.63	2	0.11
23538-1	2 10.20W	62 00.60	1667	1.32	>250 m	35.2	7.1	0.87	7	0.39
23540-2	2 30.60W	62 46.20	1126	1.19	>250 m	35.1	5.8	0.60	4	0.04
HM94-12	3 33.00W	71 19.20	1816	0.63 <sup>*)</sup>	150–200 m	35.0	2.4	0.36	2	0.09
HM94-18	5 42.00W	74 30.00	2469	0.52 <sup>*)</sup>	150–200 m	35.0	4.0	0.48	3	0.20
Nordic Seas (Arctic Domain and polar waters) core top samples										
23231-2	3 59.40W	78 54.00	1979	0.17	0–50 m	34.0	0.2	0.43	2	0.23
23232-1	1 37.20W	79 01.80	2642	0.64	150–200 m	34.9	1.1	0.44	2	0.03
23235-1	1 23.40E	78 52.20	2500	0.24	50–100 m	34.7	1.5	0.46	4	0.06
23347-4	16 04.80W	70 26.40	1375	−0.05	0–50 m	33.8	1.4	0.53	3	0.02
23348-2	18 57.00W	70 25.20	737	−0.33	0–50 m	33.3	0.5	0.56	2	0.13
23506-1	7 36.00W	72 23.40	2670	0.15	0–50 m	34.2	2.3	0.46	2	0.16
23509-1	13 30.00W	73 49.80	2576	0.11	0–50 m	33.2	0.6	0.50	6	0.08
23549-9	4 36.00W	75 03.60	3624	−0.05	0–50 m	34.1	1.6	0.47	2	0.27
PS2638-6	22 45.00W	72 05.40	428	–	0–50 m	31.7	−1.0	0.44	3	0.08

<sup>a</sup> Source: see references (Meland et al., 2006 and Simstich et al., 2003). <sup>b</sup> Average calcification depths are estimated using the  $\delta^{18}\text{O}$ -difference between shallow-dwelling *T. quinqueloba* and deep-dwelling *N. pachyderma* (sin.):  $\Delta\text{depth} = -86 + \Delta\delta^{18}\text{O} \times 300$  following the study of Simstich (1999). Negative values are set to 0–50 m. <sup>\*)</sup>  $\Delta\delta^{18}\text{O}_{\text{Nps}}$  ratios from adjacent cores 23277 and 23254, see Simstich et al. (2003). <sup>c</sup> Summer salinities and SSTs are averaged using depth corresponding hydrographic data from July–September (main planktonic bloom in the Nordic Seas (Kohfeld et al., 1996)) from the World Ocean Atlas, NOAA, 2001 ([http://www.nodc.noaa.gov/OC5/WOA01/pr\\_woa01.html](http://www.nodc.noaa.gov/OC5/WOA01/pr_woa01.html)). <sup>d</sup>  $\delta^{44/40}\text{Ca}$  values are given in [‰] relative to NIST SRM 915a. <sup>e</sup> Number of repeated measurements of each sample. <sup>f</sup>  $2\text{SEM} = 2\sigma/n^{0.5}$ .

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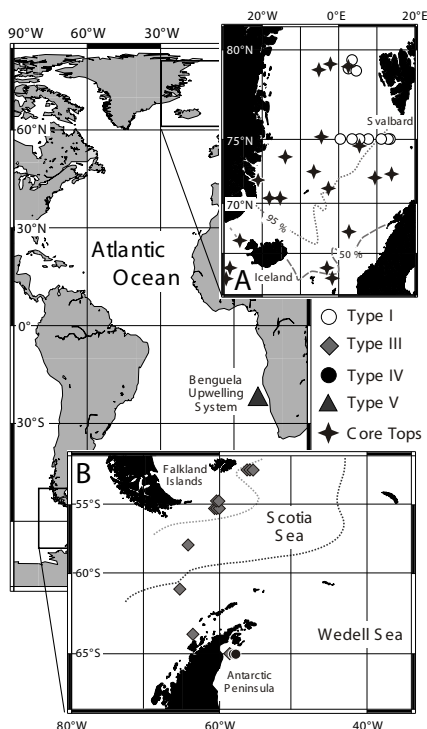
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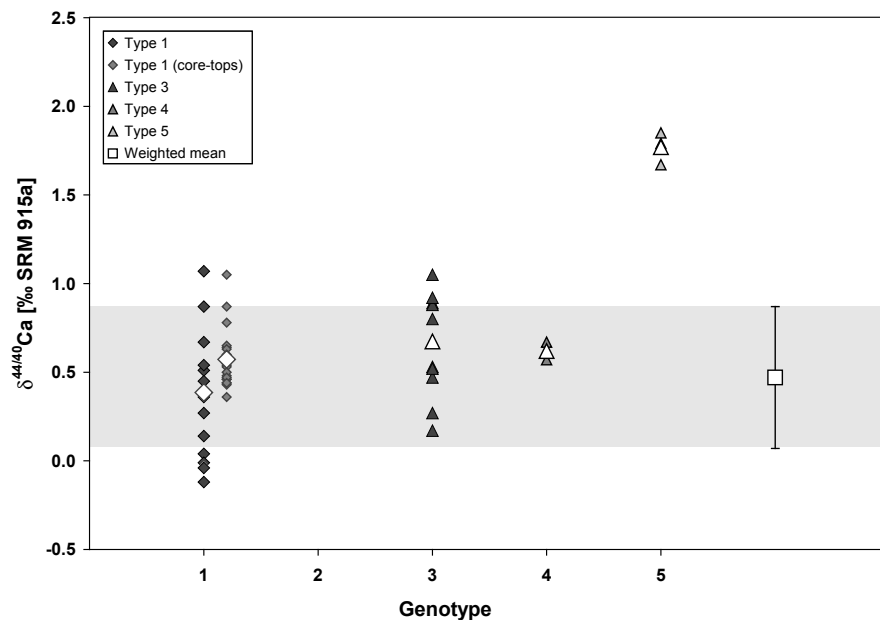


**Fig. 1.** Sampling localities of genotyped and core-top samples of left-coiling (sin.) *N. pachyderma*. (Inlet A) Sampling localities of *N. pachyderma* (sin.) Type I (open circles) and core-top sites (stars) in the northern North Atlantic. The contours denote the sediment “core-top” coiling ratio (% sin coiling), delineating the modern *N. pachyderma* (sin.) province (Pflaumann et al., 1996). (Inlet B) Sampling sites of *N. pachyderma* (sin.) Type III and IV in the subpolar/polar Antarctic. The contours delineate the approximate position of the Subantarctic Front (grey) and the Polar Front (black). The main map highlights the sampling site of *N. pachyderma* (sin.) Type V from the Benguela upwelling system.

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**Fig. 2.** Genotypes of *N. pachyderma* (sin.) vs. Ca isotope composition showing that genotype has a no significant effect on  $\delta^{44/40}\text{Ca}$ . The mean  $\delta^{44/40}\text{Ca}$  values for genotype I, III and IV are within uncertainties indistinguishable from each other, and are best expressed by the overall weighted average (grey-shaded bar).

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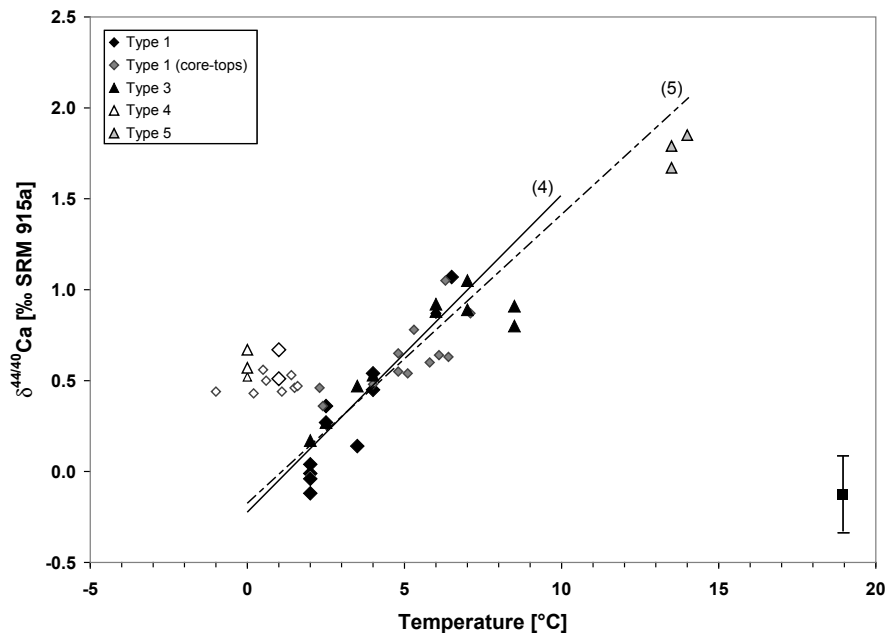
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**Fig. 3.** Ca isotope composition of genotyped (diamonds) and core-top (triangles) *N. pachyderma* (sin.) in relation to measured and calculated ambient seawater temperature. Closed symbols highlight samples from open marine settings. Samples from the “cold-end” ( $T=2.0\pm0.5^{\circ}\text{C}$  and  $\text{SAL}=33.0\pm0.5\%$ ) are shown in open symbols. The  $\delta^{44/40}\text{Ca}$  temperature relationships (4, black line) and (5, dashed line) are further shown, with temperature gradients of  $0.17\text{‰}/^{\circ}\text{C}$  and  $0.16\text{‰}/^{\circ}\text{C}$ , respectively. The error bar for  $\delta^{44/40}\text{Ca}$  is given in the right corner.

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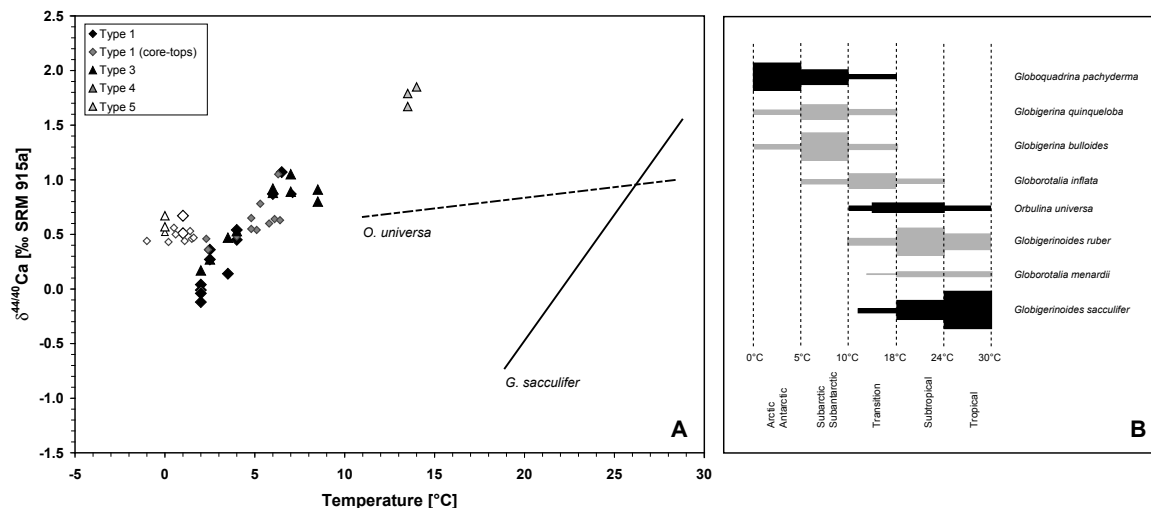
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**Fig. 4.** Comparison of the temperature sensitivity between three planktonic foraminifera species, *N. pachyderma* (sin., this study), *G. sacculifer* (Hippler et al., 2006) and *O. universa* (Gussone et al., 2003) obtained in systematic calibration studies **(A)** and their preferred sea surface temperature habitats **(B)**. Width of lines indicates relative abundance (modified from Boersma, 1978).

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